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**Invited paper**

# Pump–probe spectroscopy of J-aggregates: a way to measure intermolecular correlations in the frequency disorder

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**Abstract**

We show that two-color pump–probe experiments yield an ideal opportunity to obtain independent information on the size and the degree of intermolecular correlation of the frequency disorder in molecular J-aggregates. Our general approach is based on the motional narrowing treatment of the disorder and may be applied to other nonlinear optical techniques as well.

## 1. Introduction

Currently, much interest exists in the optical properties of molecular J-aggregates. J-aggregates are mesoscopic assemblies of molecules which are bound by electrostatic forces. Due to transfer interactions between the optical transitions of the various molecules, the eigenstates (Frenkel excitons) are delocalized over the assembly, which gives rise to interesting collective effects in the optical response of the aggregate. Examples are motional line narrowing [1], exciton superradiance [2], and the occurrence of giant nonlinear polarizabilities [3]. It is by now well established that disorder in the molecular transition frequencies is an important factor in the observed optical response, as it limits the delocalization of the eigenstates and thereby reduces the size enhancement of the spontaneous emission rate [4] and the nonlinearities [5]. For the linear J-aggregates of pseudoisocyanine (PIC) in a glassy host, linear [4] and nonlinear [6] optical experiments have so far been found consistent with an exciton delocalization range of 50 molecules; the underlying molecular disorder has a standard deviation of $64\,cm^{-1}$, which is to be compared with a nearest-neighbor interaction of roughly $-600\,cm^{-1}$.

Characteristic for J-aggregates is the sharp J-band in the absorption spectrum [2]. The sharpness is usually attributed to motional narrowing of the molecular inhomogeneities: A delocalized exciton state averages over the random frequencies of the individual molecules within an aggregate. If the random components of the transition frequencies of the molecules in an aggregate are mutually uncorrelated, the absorption band is narrowed by a factor of roughly $\sqrt{N}$, where $N$ is the (coherence) size of the aggregate [1]. This scaling may, for instance, be used to estimate $N$ from the width of the J-band [2]. It is an open question, however, whether intermolecular correlations in the disorder are absent. In fact, for closely spaced molecules,


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which are perturbed by roughly the same environment, such correlations seem very likely. If correlations exist, the narrowing factor will be less than $\sqrt{N}$ [1]. In practice, it is impossible to obtain independent information of the magnitude and the degree of correlation of the energetic disorder from the linear absorption spectrum: strong disorder and weak correlations may result in the same J-band width as weak disorder and strong correlations. Therefore, no estimates of intermolecular disorder correlations within aggregates are known so far, which amounts to a serious lack of knowledge about these systems. In this paper, we show how information on these correlations can be obtained from two-color pump–probe experiments.

## 2. Aggregate model and the pump–probe spectrum

We consider an ensemble of noninteracting disordered aggregates. Each aggregate is modeled as a linear chain of $N$ equidistant nonpolar two-level molecules with parallel transition dipoles of magnitude $\mu$. The electronic states of an aggregate are described by the standard Frenkel exciton Hamiltonian [7].

$$\hat{H}_0 = \hbar \sum_{n=1}^{N} (\omega_0 + d_n)\hat{B}_n^\dagger \hat{B}_n + \hbar \sum_{n=1}^{N-1} V(\hat{B}_n^\dagger \hat{B}_{n+1} + \hat{B}_{n+1}^\dagger \hat{B}_n) \equiv \hbar \sum_{n,m} H_{nm} \hat{B}_n^\dagger \hat{B}_m. \quad (1)$$

Here $\hat{B}_n$ and $\hat{B}_n^\dagger$ denote the Pauli annihilation and creation operators for an excitation on molecule $n$, respectively, and $\omega_0 + d_n$ is the transition frequency of molecule $n$, where $\omega_0$ is the average transition frequency and $d_n$ is a static random offset which describes diagonal disorder. Finally, $V$ is the nearest-neighbor interaction, which is negative for J-aggregates. $V$ is assumed to be homogeneous.

As disorder model, we allow for a general Gaussian multivariate distribution for the frequency offsets $d_1, \ldots, d_N$ within an aggregate. The first moments of this distribution vanish, whereas for the second moments we assume covariances of the form

$$\langle d_n d_m \rangle = a_0^2 \exp[-|n-m|/l_0]. \quad (2)$$

This distribution is identical to the one used by Knapp in his analysis of the linear absorption spectrum of J-aggregates [1]. $a_0$ gives the magnitude of the molecular disorder and $l_0$ is the correlation length of the disorder in units of the lattice constant. Note that $a_0$ equals the standard deviation $\langle d_n^2 \rangle^{1/2}$ of the Gaussian distribution for the frequency offset of molecule $n$ regardless of the values of the other frequencies. Eq. (2) interpolates continuously between completely uncorrelated inhomogeneities for $l_0 \to 0$ and infinitely strong correlations for $l_0 \to \infty$. In the latter case all molecules within one aggregate have the same transition frequency, which is randomly chosen from a Gaussian with standard deviation $a_0$.

In order to calculate the optical response of the aggregates, we need the eigenstates of the Hamiltonian Eq. (1). Because $\hat{H}_0$ conserves the number of excitations, the eigenstates separate into classes of linear combinations of states with a fixed number of molecules excited: exciton bands (Fig. 1). Using the Jordan–Wigner transformation, all $2^N$ eigenstates of $\hat{H}_0$ can be obtained by only diagonalizing the tridiagonal $N \times N$ matrix $H_{nm}$, irrespective of the disorder [8]. Let the normalized eigenvectors of $\hat{H}_0$ (for a particular realization of the disorder) have components $\varphi_{kn}$ and eigenvalues $\Omega_k$ ($k = 1, \ldots, N$). Then, the ground state of the aggregate is the state in which all molecules are in their ground state. The one-exciton band consists of $N$ states in which the molecules share one excitation (the conventional Frenkel excitons). In the site representation, these states have the form

$$|k\rangle = \sum_{n=1}^{N} \varphi_{kn} |n\rangle, \quad (3)$$

where $|n\rangle$ is the state in which only molecule $n$ is excited. The frequency of $|k\rangle$ is $\Omega_k$. The two-exciton band contains $N(N-1)/2$ states in which the molecules share two excitations. These may be written $|k_1, k_2\rangle$ ($k_1 > k_2$) and have site representation

$$|k_1, k_2\rangle = \sum_{\substack{n_1, n_2 = 1 \\ (n_2 > n_1)}}^{N} (\varphi_{k_1 n_1}\varphi_{k_2 n_2} - \varphi_{k_1 n_2}\varphi_{k_2 n_1}) |n_1, n_2\rangle, \quad (4)$$

where $|n_1, n_2\rangle$ denotes the state with molecules $n_1$ and $n_2$ excited. The frequency of this state is

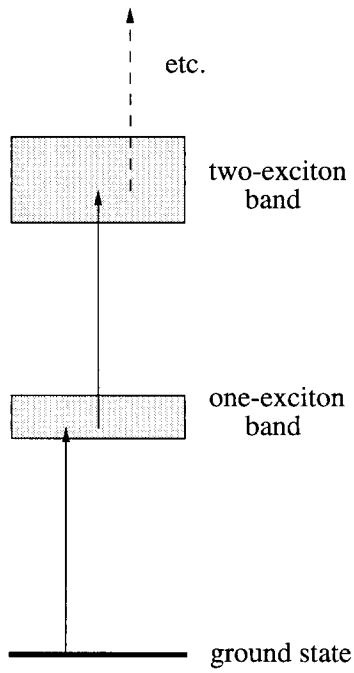


Fig. 1. Schematic representation of the lower part of the energy level scheme of an aggregate of two-level molecules. The excited states occur in exciton bands, in which the total number of excitations shared by the molecules is a constant. The separation between consecutive bands is of the order of the average molecular transition frequency. Optical transitions are only allowed between adjacent bands.

given by $\Omega_{k_1k_2} = \Omega_{k_1} + \Omega_{k_2}$, which is simply the sum of two one-exciton frequencies. Higher exciton states can be characterized in an analogous way [8] but we will not need these states in this paper. It should be stressed that two-exciton states are not direct products of two one-exciton states. We finally note that optical transitions can only occur between states in two adjacent exciton bands.

We now turn to the description of the two-color pump–probe spectrum of these aggregates. In a pump–probe experiment, the sample is first excited by a short laser pulse of center frequency $\omega_1$; a variable delay time $\tau$ later, the state of the sample is probed by a laser with frequency $\omega_2$. The differential absorption spectrum, $\Delta A(\omega_1, \omega_2; \tau)$, is defined as the difference between the probe absorption with and without pump pulse. To lowest order in the laser intensities, this spectrum measures third-order optical response functions [9]. However, if the delay is long compared to the pulse durations and the dephasing time of the coherences between and inside the exciton bands, the experiment may be treated as a sequence of two linear absorption experiments. First, linear absorption of the pump pulse creates one-excitons. During the delay time, the one-excitons can decay to the ground state or redistribute over the one-exciton band through scattering on phonons. Finally, the state of the system is probed by measuring the linear absorption of the probe pulse. As the probe absorption takes place in a prepared system, in which population has been taken away from the ground state to the one-exciton band, the differential absorption spectrum contains contributions arising from (i) stimulated emission from the one-exciton states, (ii) bleaching of the transitions from the ground state to one-exciton band, and (iii) the excitation of two-excitons.

We have derived the differential absorption spectrum within the above "sequential" picture, for pulse durations that are short compared to the exciton dephasing times. If we restrict to describing the dynamics of the one-exciton populations during the pump–probe delay by a simple exponential decay with rate $\gamma_k$, the result reads [10]

$$\begin{aligned}\Delta A(\omega_1, \omega_2; \tau) = &- C\Big\langle \sum_{k_1,k_2=1}^{N} \exp(-\gamma_{k_1}\tau) \\ &\times |\mu_{0k_1}\mu_{0k_2}|^2 (1 + \delta_{k_1,k_2}) \\ &\times \hat{I}_1(\omega_1 - \Omega_{k_1}) \hat{I}_2(\omega_2 - \Omega_{k_2}) \Big\rangle \\ &+ C\Big\langle \sum_{\substack{k_1,k_2,k_3=1 \\ k_2>k_3}}^{N} \exp(-\gamma_{k_1}\tau) \\ &\times |\mu_{0k_1}\mu_{k_1,k_2k_3}|^2 \hat{I}_1(\omega_1 - \Omega_{k_1}) \\ &\times \hat{I}_2(\omega_2 + \Omega_{k_1} - \Omega_{k_2} - \Omega_{k_3}) \Big\rangle. \end{aligned} \tag{5}$$

Here, $C$ is a constant and $\hat{I}_1(\omega)$ and $\hat{I}_2(\omega)$ denote the power spectra of the envelopes of the pump and the probe pulse, respectively. Furthermore, $\mu_{0k_1}$ is the transition dipole between the aggregate ground state and the one-exciton $|k_1\rangle$ and $\mu_{k_1,k_2k_3}$ is the

transition dipole between $|k_1\rangle$ and the two-exciton $|k_2, k_3\rangle$. These dipoles can be expressed in terms of sums over the eigenvector components $\varphi_{kn}$ [8,11]. The first part of Eq. (5) contains the contributions from stimulated emission and bleaching, which result in a negative differential absorption; the second part describes the positive absorption of photons that cause the transition from the $|k_1\rangle$ one-exciton to the $|k_2, k_3\rangle$ two-exciton. Finally, $\langle \ldots \rangle$ denotes the disorder average over the joint distribution of the molecular frequency offsets described earlier in this section.

## 3. Differential absorption spectrum in the motional narrowing limit

In order to calculate the differential absorption spectrum Eq. (5), one generally needs numerical procedures to simulate the disorder and to diagonalize $H_{nm}$. Only for homogeneous aggregates ($a_0 = 0$) it is possible to diagonalize $H_{nm}$ analytically:

$$\varphi_{kn}^0 = \sqrt{\frac{2}{N+1}} \sin\left(\frac{\pi k n}{N+1}\right), \tag{6a}$$

$$\Omega_k^0 = \omega_0 + 2V\cos\left(\frac{\pi k}{N+1}\right), \tag{6b}$$

where the superscript 0 is used to indicate quantities pertinent to the homogeneous system. A simple way to account for disorder now exists of using perturbation theory with respect to the inhomogeneous contribution $\hat{H}_{\text{pert}} = \hbar \Sigma_n d_n \hat{B}_n^\dagger \hat{B}_n$ in the Hamiltonian. For uncorrelated disorder ($l_0 = 0$), the smallness parameter for this expansion is $a_0 N^{3/2}/\pi^2 |V|$ [1]. In a lowest-order evaluation of Eq. (5), we use the eigenfrequencies to first order in $\hat{H}_{\text{pert}}$ and the unperturbed eigenstates, which implies that the transition dipoles between the exciton states are taken identical to those for the homogeneous aggregate. This approach, known as the motional narrowing limit, has provided much insight into the linear absorption spectra of J-aggregates [1].

In the motional narrowing limit, Eq. (5) can be simplified considerably, due to the fact that for homogeneous aggregates a strong concentration of oscillator strength in only a few transitions occurs. Starting from the ground state, almost the entire oscillator strength (81%) resides in the transition to the one-exciton $|k = 1\rangle$; from this state, the largest part of the oscillator strength (70%) is contained in the transition to the $|k_1 = 2, k_2 = 1\rangle$ two-exciton [11]. Therefore, the dominant features in the pump–probe spectrum are obtained by setting $k_1 = k_2 = 1$ in the first term of Eq. (5) and $k_1 = k_3 = 1$, $k_2 = 2$ in the second term. The only disorder averages that now occur in the differential absorption are $\langle \hat{I}_1(\omega_1 - \Omega_1^0 - D_1) \times \hat{I}_2(\omega_2 - \Omega_1^0 - D_1)\rangle$ and $\langle \hat{I}_1(\omega_1 - \Omega_1^0 - D_1) \times \hat{I}_2(\omega_2 - \Omega_2^0 - D_2)\rangle$, where $D_k$ is the inhomogeneous contribution to the eigenfrequency $\Omega_k$ to first order in $\hat{H}_{\text{pert}}$: $D_k = \Sigma_n |\varphi_{kn}^0|^2 d_n$. The first average requires the probability distribution $P^{(1)}(D_1)$ for $D_1$ only, whereas the second average requires the *joint* probability distribution $P^{(2)}(D_1, D_2)$ for $D_1$ and $D_2$. If these distributions are broad compared to the spectral width of the pump and probe pulses (which in practice means that the laser pulses are narrow compared to the J-band), we arrive at [10]:

$$\begin{aligned}\Delta A(\omega_1, \omega_2; \tau) = & -2C\exp(-\gamma_1 \tau)|\mu_{01}^0|^4 \\ & \times P^{(1)}(\omega_1 - \Omega_1^0) \\ & \times \Bigg\{ [\hat{I}_1 * \hat{I}_2](\omega_1 - \omega_2) \\ & - \frac{|\mu_{1,21}^0|^2}{2|\mu_{0,1}^0|^2} P^{(c)}(\omega_2 - \Omega_2^0 | \omega_1 \\ & - \Omega_1^0) \hat{I}_1 \hat{I}_2 \Bigg\}. \end{aligned} \tag{7}$$

Here, * indicates a convolution, $\hat{I}_1$ and $\hat{I}_2$ are the total pump and probe intensity, respectively, and $P^{(c)}(D_2|D_1) \equiv P^{(2)}(D_1, D_2)/P^{(1)}(D_1)$ denotes the conditional probability for the inhomogeneous frequency offset of the $|k = 2\rangle$ one-exciton, given the frequency offset of the $|k = 1\rangle$ one-exciton. As is evident from Eq. (7), the overall *magnitude* of the pump–probe signal is determined by the absorption of the pump pulse ($P^{(1)}(\omega_1 - \Omega_1^0)$ represents the J-band in the motional narrowing limit [1,10]) and the exponential decay during the delay time. The *shape* of the pump–probe signal is determined

by the factor in curly brackets in Eq. (7). For narrow pulses, a bleach (and stimulated emission) will be observed at frequency $\omega_2$ only if the pump and probe pulses overlap, which explains the convolution. Extra absorption is observed at $\omega_2$ only if the probe pulse is resonant with the transition from the $|k=1\rangle$ one-exciton to the $|k_1=2,\ k_2=1\rangle$ two-exciton in aggregates that have their $|k=1\rangle$ one-exciton frequency resonant with the pump pulse. This explains the conditional probability. For J-aggregates, $\Omega_2^0 > \Omega_1^0$, so that the extra-absorption peak will be blue shifted relative to the bleaching feature.

For the disorder model introduced in Section 2, both $P^{(1)}(D_1)$ and $P^{(2)}(D_1, D_2)$ are Gaussian with vanishing first moments and covariances that can be derived from the molecular covariances Eq. (2) [10]:

$$B_{kk'} \equiv \langle D_k D_{k'} \rangle = \left(\frac{a_0}{N+1}\right)^2 \left\{ (N+1)\frac{1+\beta}{1-\beta} - 2(1-\beta^{N+1}) f(k) f(k') + \frac{1}{4}(N+1)(1-\beta^2) \times \left[\frac{1}{g(k)} + \frac{1}{g(k')}\right] \times [\delta_{k,k'} + \delta_{k+k',N+1}] \right\}, \tag{8a}$$

where

$$f(k) = \frac{1}{1-\beta} - \frac{1-\beta\cos[2\pi k/(N+1)]}{1-2\beta\cos[2\pi k/(N+1)]+\beta^2}, \tag{8b}$$

$$g(k) = 1 - 2\beta\cos[2\pi k/(N+1)] + \beta^2. \tag{8c}$$

Here, we have introduced the parameter $\beta \equiv \exp(-1/l_0) = \langle d_n d_{n+1} \rangle / \langle d_n^2 \rangle$, which gives the degree of correlation between the transition frequencies of the molecules within one chain. $\beta$ ranges from 0 (no correlations) to 1 (perfect correlations). From Eq. (8), we find that $P^{(1)}(D_1)$, the J-band line shape, is Gaussian with vanishing mean and width (standard deviation) $\sigma_1 = \sqrt{B_{11}}$. $\sigma_1$ is proportional to $a_0$, but also is a function of $\beta$, and continuously varies from $\sigma_1 = a_0[2(N+1)/3]^{-1/2}$ for $\beta = 0$ (motional narrowing) to $a_0$ for $\beta = 1$ (no narrowing). It is therefore impossible to obtain independent information on the magnitude and the degree of correlation of the molecular disorder from the linear absorption spectrum. From $P^{(1)}(D_1)$ and $P^{(2)}(D_1, D_2)$, the conditional probability $P^{(c)}(D_2|D_1)$ is also found to be Gaussian with mean $(B_{12}/B_{11})D_1$ (which in general does not vanish, as $\langle D_1 D_2 \rangle \neq 0$) and standard deviation $\sigma_{12}^c = [B_{22} - B_{12}^2/B_{11}]^{1/2}$.

We will now further analyze the differential absorption spectrum (Eq. 7). The maximum of the bleach occurs (for symmetric pulse shapes) at $\omega_2 = \omega_1$, while the maximum of the extra absorption occurs at the mean value of $P^{(c)}(\omega_2 - \Omega_2^0 | \omega_1 - \Omega_1^0)$, i.e. at $\omega_2 - \Omega_2^0 = (\omega_1 - \Omega_1^0)\, B_{12}/B_{11}$. Thus, the frequency separation between the absorption and bleach peaks is given by

$$\Delta_{\text{abs, bl}} = \alpha(\omega_1 - \Omega_1^0) + (\Omega_2^0 - \Omega_1^0), \tag{9}$$

with $\alpha \equiv B_{12}/B_{11} - 1$. We first note that if the pump is tuned to the maximum of the J-band ($\Omega_1^0$), $\Delta_{\text{abs, bl}}$ equals $\Omega_2^0 - \Omega_1^0$, which may be used to obtain the size $N$ of the aggregate (Eq. (6b)). Furthermore, using Eq. (8), we find that the factor $\alpha$ varies between $-1/3$ ($\beta = 0$) and 0 ($\beta \to 1$). The full $\beta$-dependence of $\alpha$ has been plotted in Fig. 2 for various aggregate sizes. The interesting point is that $\alpha$ does not depend on $a_0$. Thus the *separation* between the extra absorption and the bleach as a function of the detuning of the pump frequency from the J-band maximum, $\omega_1 - \Omega_1^0$, gives direct

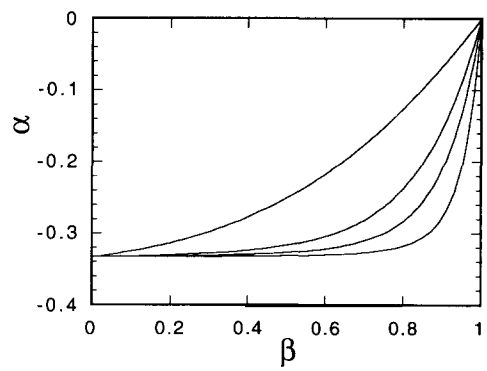


Fig. 2. The slope $\alpha$ defined in Eq. (9) as a function of the degree of intersite correlation $\beta$. From top to bottom, the curves apply to aggregates of $N = 10, 30, 50$, and 100 molecules, respectively.

information on $\beta$ alone. By contrast, the *width* $\sigma_{12}^{c}$ of the extra absorption peak depends on both $\beta$ and $a_0$. If $\beta$ is known from measuring $\alpha$, the width of the extra-absorption peak can thus be used to obtain $a_0$.

## 4. Discussion

In this paper, we have calculated the pump–probe spectrum for linear J-aggregates. We have shown that, in contrast to linear absorption measurements, two-color pump–probe experiments can be used to obtain separate information on both the magnitude and the degree of correlation of the molecular frequency disorder within aggregates. A limitation of our result is that it has been derived within the motional narrowing limit, which treats the disorder in a perturbative way. It should be noted, however, that for strong correlations ($\beta \to 1$) our results become exact, as then each individual aggregate is homogeneous. In that case, a perfect correlation exists between all the one- and two-exciton frequencies of each aggregate, and the slope $\alpha$ defined in Eq. (9) rigorously vanishes ($\Delta_{\mathrm{abs,bl}} = \Omega_2^0 - \Omega_1^0$, independent of $\omega_1$). An alternative experimental indication for the existence of strong correlations would be the fact that the extra-absorption peak is much narrower than the J-band; in the limit $\beta \to 1$, the width of the extra-absorption peak is only limited by the spectral width of the laser pulses [10]. If the disorder correlations are not strong, the validity of the perturbative approach is limited by the fact that for strong disorder ($a_0$) and (or) large chain lengths ($N$), the exciton states are localized on parts of the chain [4]. A heuristic procedure to still put our results to use, is to replace the chain length $N$ in all expressions by the typical delocalization length of the excitons at the J-band. It has recently been shown that, using the delocalization length obtained from linear optical experiments, this procedure (with no free parameters) yields an excellent description of the pump–probe spectrum of PIC aggregates when pumped at the center of the J-band [6]. In addition, it is noteworthy that preliminary results of full numerical simulations of the pump–probe spectrum Eq. (5) reveal a clear dependence of the slope $\alpha$ on the degree of disorder correlation, even if the disorder is too strong to justify a perturbative approach. Thus, also under realistic circumstances, two-color pump–probe experiments provide a promising tool to measure intermolecular correlations in the frequency disorder.

We finally note that Eq. (8) suffices to calculate the joint probability distribution for an arbitrary set of exciton frequencies [10], which makes it possible to also treat any other nonlinear optical technique within the motional narrowing limit.

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